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# Pilot-Plant Investigations of the Adsorption of 1,2-Dichloroethane and 1,2-Dibromo-3-Chloropropane from Water Supplies

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# PILOT-PLANT INVESTIGATIONS OF THE ADSORPTION OF 1,2-DICHLOROETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE FROM WATER SUPPLIES

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# PILOT-PLANT INVESTIGATIONS OF THE ADSORPTION OF 1,2-DICHLOROETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE FROM WATER SUPPLIES

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## ABSTRACT

This research considers the results of granular activated carbon (GAC) pilot-plant studies related to the adsorption of an industrial solvent and a pesticide, namely, 1-2-dichloreothane (DCE), and 1,2-dibromo-3-chloropropane (DBCP), respectively, from river water. A predictive mathematical model [Michigan Adsorption Design and Application Model-MADAM-film/particle diffusion version (1-4)] which has demonstrated potential for use in the design and operation of GAC for wastewater treatment, was used in simulation and prediction of the dynamic performance of fixed-bed pilot-plant adsorbers. Good agreement between the predicted breakthrough profiles and the pilot-plant verification data was observed.

## EXPERIMENTAL APPROACH

### Materials and Methods

Carbon Type. 12 x 40 US standard sieve size Filtrasorb® 400 (Calgon Corp., Pittsburgh, PA)*. Carbon particle sizes larger than 12 mesh were screened out and discarded; less than 5% of the particles were smaller than 40 mesh. The carbon that was used for small scale testing was washed with organic free water, dried at 105°C and stored in air-tight screw cap bottles.

*Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

Background Solution. Cincinnati Water Works unchlorinated effluent from a 3-day detention reservoir which is fed with "alum dosed" Ohio River water. [Average total organic carbon (TOC) was 1.45 mg/L].

Analysis. Analyses for DCE were performed using a purge and trap method similar to that described by Bellar and Lichtenberg (5); 1,2-dichloropropane was used as an internal standard. For DBCP analysis, a modification of the purge and trap (Tekmar Model LSC-1 Liquid Sample Concentrator; Cincinnati, OH) was employed. The gas chromotograph detector response was recorded graphically, and peak area printouts were used to measure concentrations.

## Adsorption Procedures

Batch Studies. Completely mixed batch reactor (CMBR) equilibrium studies for DCE were conducted using the static bottle-point technique. Different quantities of unpulverized activated carbon were placed in 250-mL bottles. The bottles were filled with spiked settled river water (SRW), sealed with teflon-lined caps, and tumbled until equilibrium was achieved.

CMBR rate studies for DCE were conducted in 1.7 liter (total volume) Celstir® bottles (Wheaton Scientific; Millville, NJ) equipped with suspended magnetic stirrers. The bottles were filled, headspace free, with spiked SRW. Weighed quantities of carbon were transferred to the reactors and the solutions stirred at 500 rpm. Samples of 5-mL volume were withdrawn periodically for analysis and unspiked SRW was added to reestablish a headspace-free condition.

Pilot-Column Studies. Column studies were performed for DCE and DBCP in 4-cm ID glass columns containing 400 grams of 12 x 14 mesh carbons. All tubing and connections were constructed of glass, stainless steel, or Teflon® . Glass sampling ports, extending into the center of the column, were provided at various depths and were equipped with Teflon® stop-cocks.

Settled Ohio River Water (SRW) was transported from the Cincinnati Water Works and stored in a large tank outside the building. The water in the storage tank was continuously recirculated with pump to prevent stagnation. The flow from the storage tank to a 100-gallon stainless steel tank inside the laboratory was controlled by the needle value to deliver a slightly greater volume than was required by the column experiments; the excess was overflowed to waste.

A concentrated solution of the test compound was contained in an air-tight 20-L glass bottle. To prevent loss by volatilization, a Teflon® bag was attached to the bottle. The bag would expand as fresh spike solution was added, or contract as solution was withdrawn. The spike solution was injected into the discharge tubing of the SRW pump. Mixing was provided by a small glass column filled with beryl saddles. The pressure drop across the adsorber was measured using a mercury manometer. Figure 1 illustrates the experimental apparatus and arrangement. The salient features of the pilot column investigations are summarized in Table 1.

## RESULTS AND DISCUSSION

### Adsorption Equilibrium

Several theoretical and empirical equations, including the Freundlich, Langmuir, and three-parameter isotherms, were investigated for the mathematical description and quantification of the DCE adsorption equilibrium data. The experimental data correlated best with the Freundlich and three-parameter isotherms. However, the Freundlich isotherm was found to be superior to the three-parameter model because of simpler and more efficient parameter estimation. The Freundlich equation relates the amount of solute adsorbed on carbon, $q_e = \log K_f + 1/n \log C_e$, where $K_f$ and $1/n$ are indicators of adsorption capacity and adsorption intensity, respectively (6). Figure 2 demonstrates the equilibrium data and Freundlich isotherm for DCE.

### Adsorption Rates

The MADAM model (1-4) was used for the estimation of mass transfer coefficients for DCE simultaneously from the CMBR rate data. To minimize the program search for the appropriate values of the film transfer coefficient, $k_{f,b}$, and the intraparticle diffusion coefficient, $D_s$, a close control value for $k_{f,b}$ was estimated by conducting a separate CMBR rate experiment using a large amount of carbon to nearly deplete the solute within the first few minutes of the experiment (7). The $k_{f,b}$ value was then calculated from the slope of the regression line for the initial rate data. Figure 3 illustrates the results of simulation analysis for a two-parameter search. The estimated coefficients, $k_{f,b} = 4.05 \times 10^{-3}$ cm/sec and $D_s = 1.77 \times 10^{-9}$ cm$^2$/sec, were used to predict the experimental profile represented by the solid line.

### Adsorption Columns

Simulation modeling analysis for DCE were conducted for three sets of experimental conditions. Table 2 summarizes values for the physical and chemical parameters associated with these studies, including values for the surface diffusion coefficient, $D_s$, and the column film transfer coefficient, $k_{f,c}$. The surface diffusion coefficient was estimated from the CMBR rate tests, and the film transfer coefficients by a correlation technique proposed by Williamson *et al* (8).

Experimental data and the predicted breakthrough profile for a typical fixed-bed pilot-plant adsorber are presented in Figure 4. The MADAM model was generally able to simulate and predict the performance of fixed-bed adsorbers for removal of DCE.

### Biodegradation Studies

All column experiments in this study exhibited biological activity. Biological growth was apparent in each column within a few days from the onset of operation.

Adsorber run 1 was the first to be conducted in an attempt to investigate the characteristic breakthrough profiles. After reaching exhaustion, the adsorber column was emptied and recharged with fresh

TABLE 1

| Adsorber Run# | Test Compound | Flowrate (mL/min) [hydraulic loading (liter/min/$m^2$)] | Avg. Soln. Conc. (µg/L) | EBCT* (min) | Total run time (days) |
|---|---|---|---|---|---|
| 1 | DCE | 100[80] | 112 | 10 | 82 |
| 2 | DCE | 100[80] | 89 | 10 | 88 |
| 3 | DCE | 50[40] | 196 | 20 | 88 |
| 4 | DCE | 200[160] | 21 | 5 | 88 |
| 5 | DBCP† | 100[80] | 18 | 10 | 166 |

†SRW was used for the first 40 days of operation and tap water was used for the remainder of the run.

* EBCT: Empty Bed Contact Time

TABLE 2. PARAMETERS USED FOR FIXED-BED ADSORBER PREDICTIVE BREAKTHROUGH PROFILES FOR DCE

| Adsorber Run # | $\bar{C}_{in}$ | d | L | Y | v | $k_{f,c}$ | $D_s$ |
|---|---|---|---|---|---|---|---|
| 1 | 112 | 0.106 | 80 | 0.4 | 0.33 | $2.6 \times 10^{-3}$ | $1.77 \times 10^{-9}$ |
| 3 (Figure 4) | 200 | 0.106 | 80 | 0.4 | 0.17 | $2.05 \times 10^{-3}$ | $1.77 \times 10^{-9}$ |
| 4 | 20 | 0.106 | 80 | 0.4 | 0.66 | $3.29 \times 10^{-3}$ | $1.77 \times 10^{-9}$ |

MERL Reported Parameters

$\bar{C}_{in}$ : average influent concentration (µg/L)

d : carbon particle diameter (cm)

L : bed length (cm)

Y : bed porosity (dimensionless)

v : interstitial velocity (cm/sec)

EBCT: empty bed contact time (min)

MADAM Determined Parameters

$k_{f,c}$ : column film transfer coefficient (cm/sec)

$D_s$ : intraparticle diffusion coefficient ($cm^2$/sec)

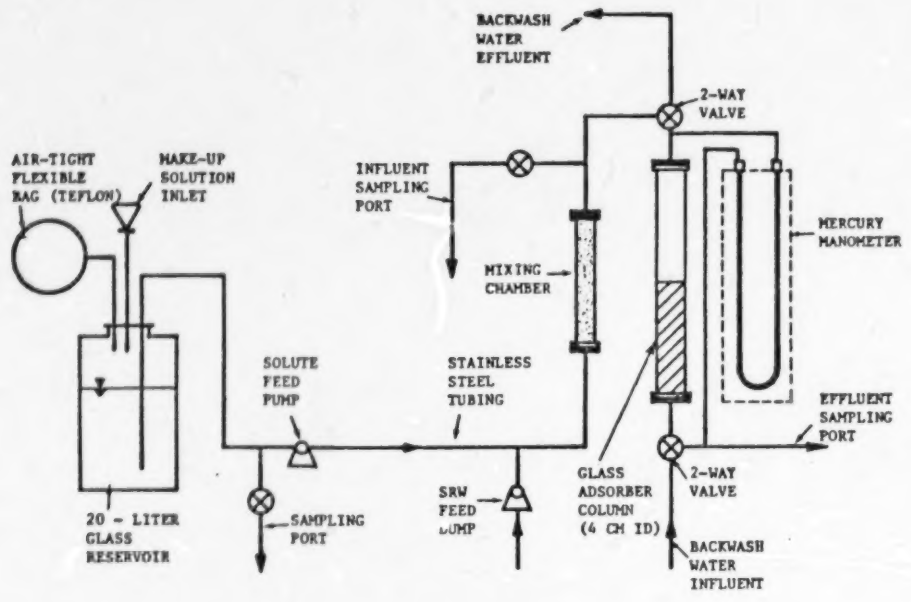


Figure 1. experimental apparatus for fixed-bed adsorber studies.

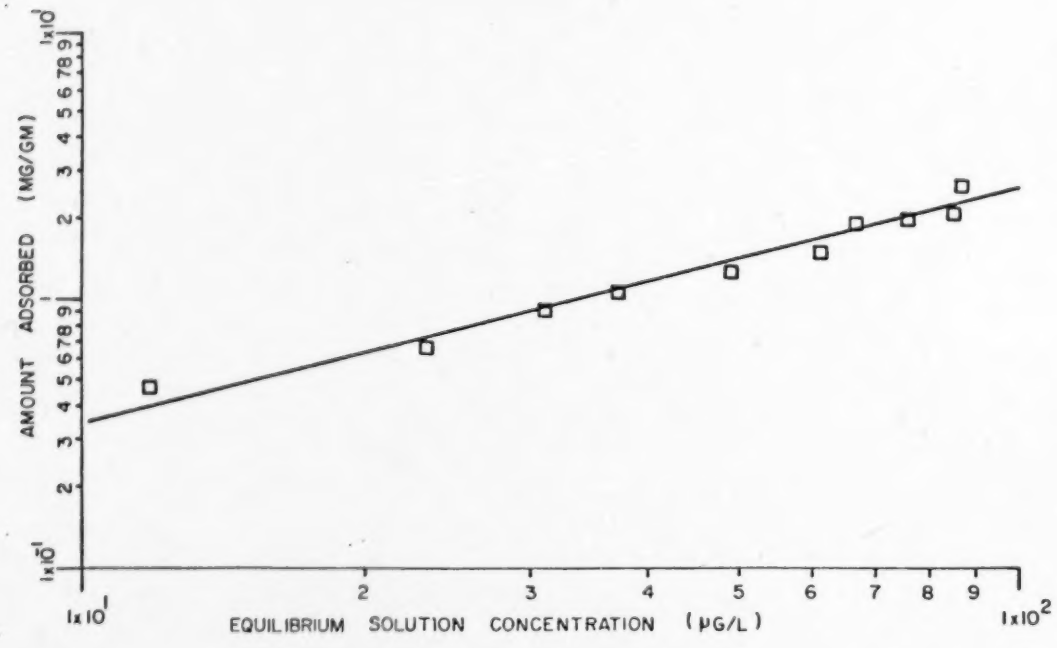


Figure 2. experimental data and Freundlich isotherm for DCE.

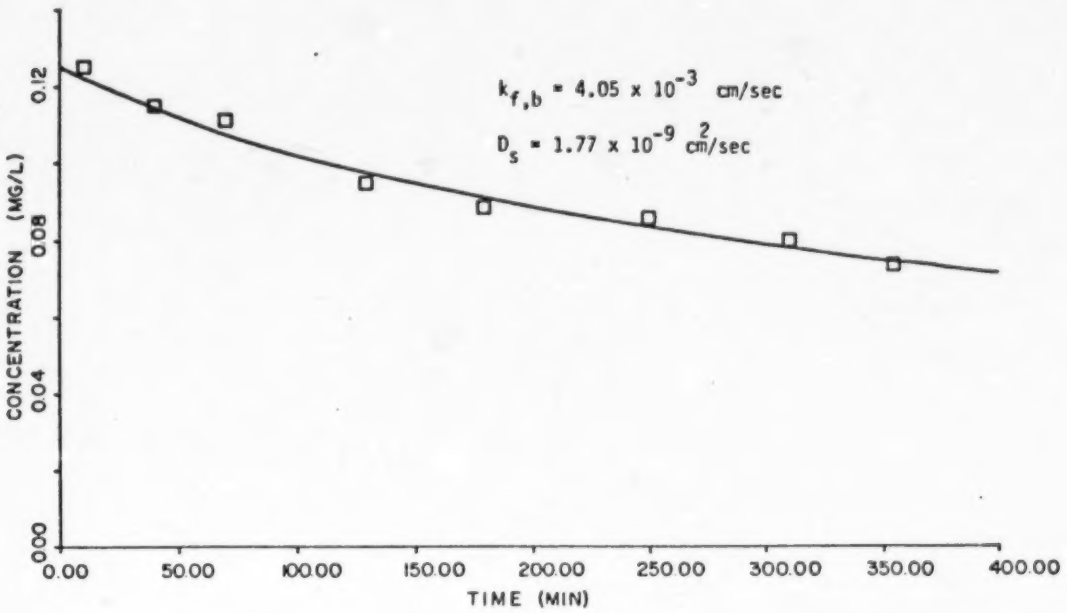


Figure 3. experimental data and model profile for rate of adsorption of DCE in a CMBR ($C_o$ = 124 µg/ℓ; 0.118 g/ℓ of 12 x 40 carbon).

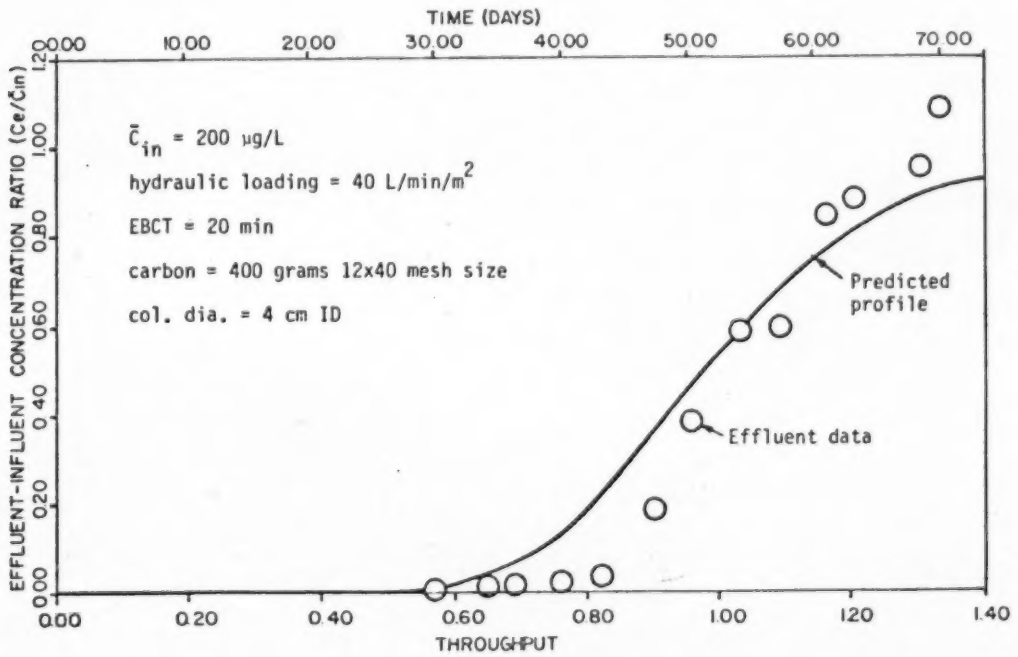


Figure 4. effluent concentration profiles for DCE (fixed-bed adsorber run 3).

activated carbon and was run (absorber run 2) in parallel with adsorber runs 3 and 4. It is of interest to note that, although adsorber runs 1 and 2 were conducted under similar conditions, no characteristic breakthrough profile was observed for adsorber run 2, as shown in Figure 5. The most logical explanation for this behavior is the unintentional seeding of adsorber run 2 by the bacteria which had been acclimated in the stainless steel column feeder tubing during an earlier run (adsorber run 1).

Figure 5 also presents the results of biodegration studies for adsorber run 4, demonstrating a decline in DCE effluent concentrations after breakthrough. It is postulated that bacterial acclimation during the initial stages of breakthrough may have been responsible for this decline. Roberts (9) reported observations for a number of trace contaminants for reclaimed water during aquifer passage. This phenomenon, however, was not experienced with adsorber runs 1 and 3. Furthermore, no breakthrough was observed for DBCP after 166 days of operation (adsorber run 5), a duration far beyond the theoretical carbon capacity (10).

That biodegradation may be responsible for removal of DCE and DBCP is not a surprising phenomenon. In fact, a recent comprehensive study reveals that almost every class of anthropogenic compounds can be degraded by some microorganisms (11). More specifically, biodegradation of DCE has been reported by Patterson and Kodukala (12). These investigators conducted static flask tests whereby the test solution was dosed with bacterial innocula from settled domestic sewage. The extent of biodegradation for DCE in these experiments was about 60%.

Evidence is available (13,14) indicating that biodegradation of trace organic materials in biofilm applications can occur in general by secondary utilization or cometabolism of secondary substrate provided that abundant primary organic substrate is available and bacteria are capable of decomposing both the primary and secondary substrates. In the present context, DCE and DBCP may be regarded as a secondary substrate while the TOC of the background solution acts as an aggregate primary substrate providing energy needed to sustain the biofilm. Figure 6 represents the TOC concentration-history profiles for adsorber runs 2 and 4, indicating a substantial decrease in the so-called "primary substrate" with an increase of EBCT during the entire course of column operation.

To investigate the extent of biodegradation of DCE in the adsorber run 2, samples were taken at various column depths and analyzed for DCE. Figure 7 shows the DCE profile after 68 days of operation, indicating extensive biodegradation within the first 2-3 cm of the column depth.

Similarly, to investigate biodegradation phenomenon for DBCP, samples were taken from various column depths at three different run times of 17, 76, and 166 days, as shown in Figure 8. The sharp initial drop in concentration within the first few centimeters of column depth would be expected for short operating times, but not after 166 days. It is thus postulated that biodegradation may be operative in the entire column depth.

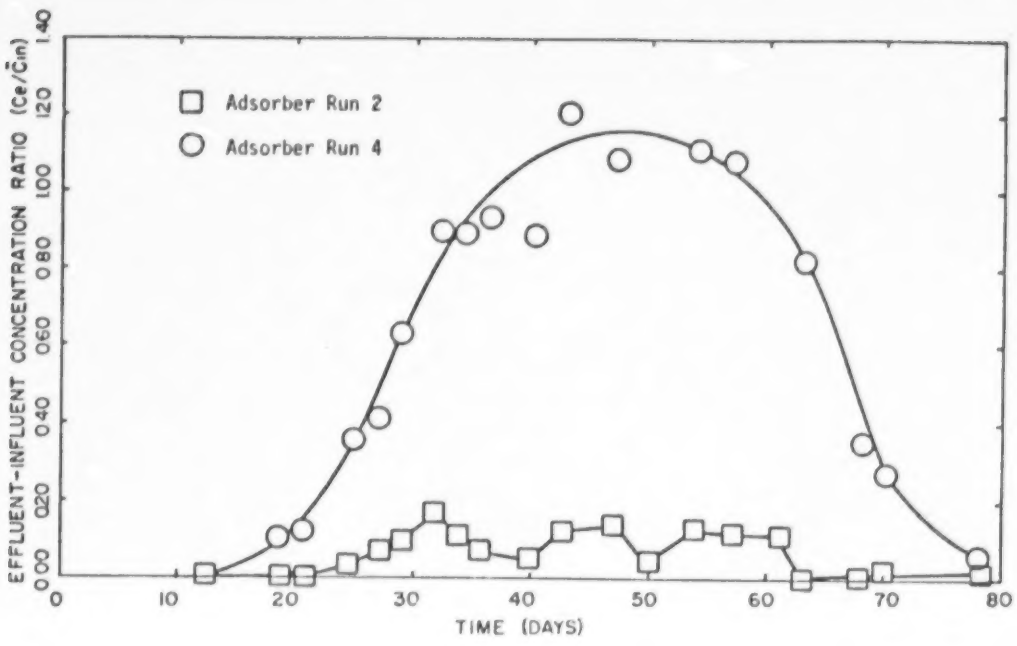


Figure 5. DCE breakthrough profiles for fixed-bed adsorber runs 2 and 4 (effect of biodegradation).

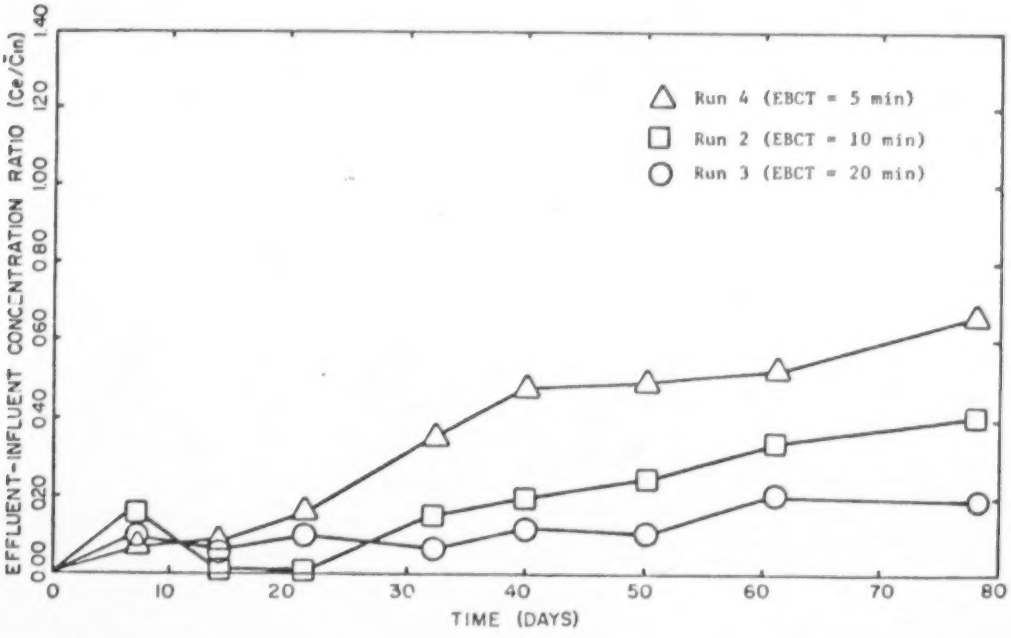


Figure 6. TOC breakthrough profiles for fixed-bed adsorber runs 2 to 4.

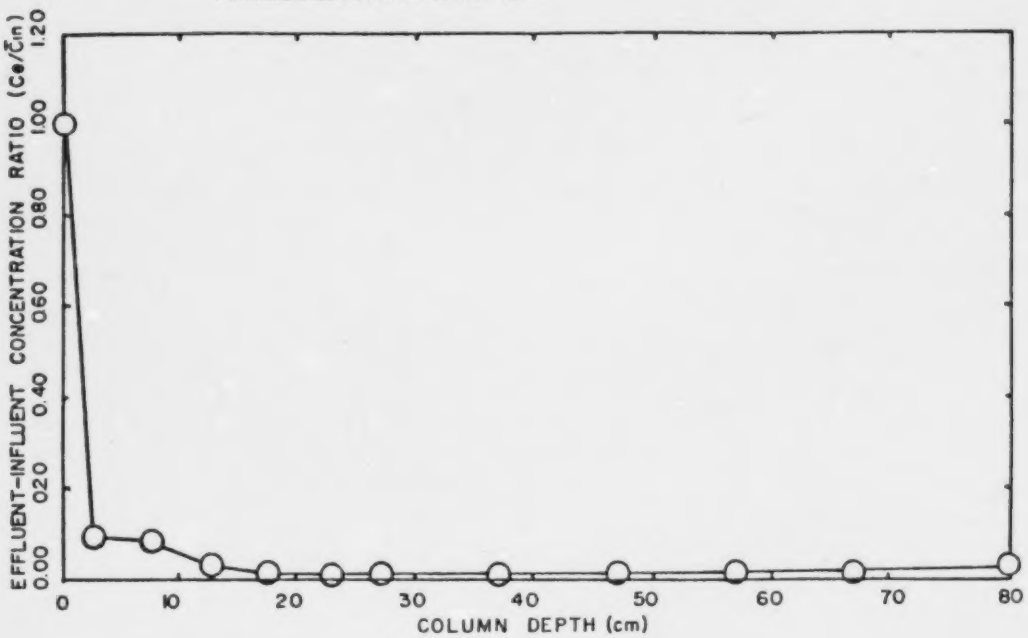


Figure 7. DCE concentration at various depths in fixed-bed adsorber run 2 after 68 days of operation.

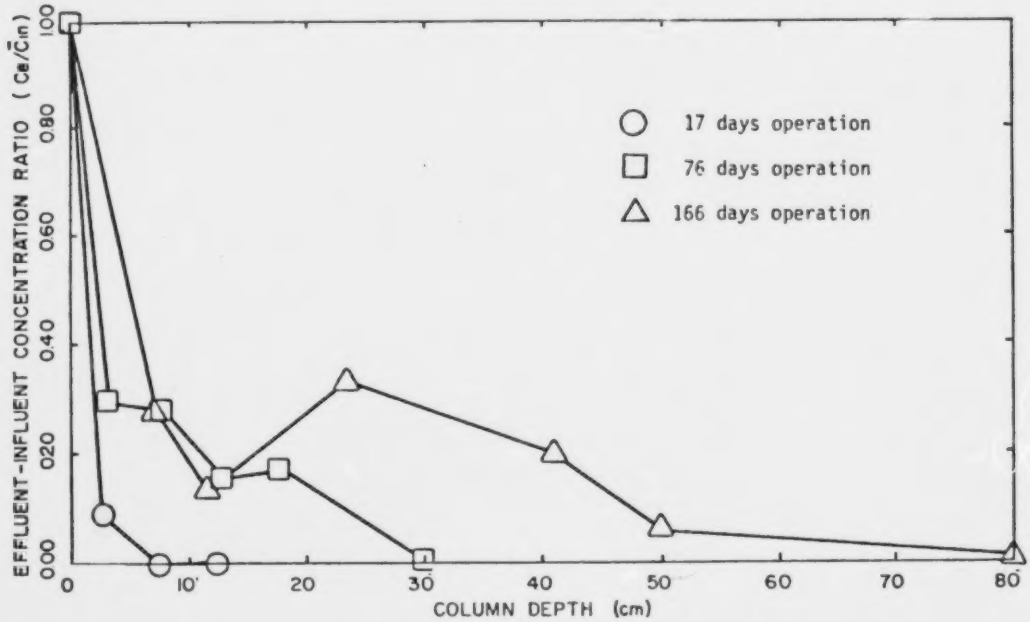


Figure 8. DBCP concentration at various depths in fixed-bed adsorber run 5 after different run times.

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